25X1A

CENTRAL INTELLIGENCE AGENCY

REPORT NO.

INFORMATION REPORT

CONFIDENTIAL

COUNTRY	Italy	DATE DISTR. 31 August 1948
SUBJECT	Preconcentration of Heavy Water in Water Electrolysis Plants	NO. OF PAGES 1
PLACE ACQUIRED	25X1A	NO. OF ENCLS. (LISTED BELOW)
DATE ACQUIRED		SUPPLEMENT TO REPORT NO. 25X1X

THIS IS UNEVALUATED INFORMATION FOR THE USE OF TRAINED INTELLIGENCE ANALYSTS

SOURCE DOCUMENTARY

Enclosed is a copy of a pamphlet entitled "Preconcentration of Heavy Water in Water Electrolysis Plants", published by Montecatini at Milan on 16 May 47.

-end-

Enclosure: "Preconcentration of Heavy Water in Water Electrolysis Plants."

DOE REVIEW COMPLETED, DEC 2001

CLASSIFICATION CONFIDENTIAL 25X1A

CONFIDENTIAL

25X1A

CPYRGHT

Milan, May 16th, 1947.

PRECONCENTRATION OF HEAVY WATER IN WATER ELECTROLYSIS PLANTS.

Heavy water concentrations remarkably above the ones in natural water, may be obtained by means of proper arrangements from industrial water electrolysis plants, so that the obtention of 100% heavy water is made possible and comparatively easy.

In this paper we describe quantitatively such preconcentration.

1. Heavy water concentration in an electrolytic cell.

If hydrogen and oxygen produced in an electrolizing cell for natural water are made to combine with each other, a synthetic water is obtained the D_2O concentration of which is below the one of the water left in the cell. During electrolysis, H_2O moleculae electrolize at higher rate than the D_2O moleculae, so that by going on with the electrolysis, the water left in the cell progressively becomes richer in D_2O; the electrolytic cell behaves in fact in a selective manner. Let be :

A   the (constant) water contents in the cell, by weight (the very slight weight increase due to the increasing percentage of D_2O is neglected);

P_e the (constant) natural water flow (by weight) feeding the cell;

x_e the (constant) concentration by weight of D_2O in the natural water feeding the cell, equal to the initial concentration of D_2O in the water of the cell;

x   the average (1) instantaneous concentration by weight (variable as function of time) of D_2O in the water of the cell;

x_1 the (constant) limit concentration by weight of D_2O in the water of the cell, such limit being reached when time equals infinite;

$r = x_1/x_e$ the "concentration ratio" ;

---

(1) Such average is intended relative to the various regions in the cell, the concentration being variable in the different points.

MOD. DJPS 4 (A 4) - 3000 2 48

a   the (constant) fraction of flow P_0 which is not electrolized and that is composed by: 1) the losses on account of overflow or the like, 2) evaporation in the room space , and 3) the steam and liquid water carried by the electrolysis produced gases;

s   the "selection ratio" (> 1) between the limit concentration x_1 and the concurrent D_2O concentration in the synthetic water which would be obtained by combining the electrolysis produced gases (for low concentrations, s is practically independent from concentration);

t   time, calculated from the beginning of the cell's operation;

e   the basis of natural logarithms ($e = 2,718 \ldots$).

      If the quantities above defined are expressed in a homogenous system of units, the heavy water balance during time dt furnishes the differential equation

$$A \; dx = x_0 \, P_0 \, dt - x \, a \, P_0 \, dt - \frac{x}{s} (\; 1-a \;) \, P_0 \, dt,$$

which, by integrating at the initial condition

$$x = x_0 \quad \text{for} \quad t = 0,$$

gives the exponential equation

$$x = x_0 \left[r - (r - 1) \; e^{-\frac{P_0}{Ar} t} \right],$$

in which r (concentration ratio) is represented by

$$r = \frac{s}{1 + a (s - 1)} \cdot$$

On the other hand, remembering that

$$x_1 = \lim_{t \to \infty} x = r \, x_0$$

we may write too

$$x = x_1 - (x_1 - x_0) \; e^{-\frac{P \, x_0}{A \, x_1} t}.$$

The speed of concentration increase is given by

$$\frac{dx}{dt} = \frac{x_0 \, P_0}{Ar} (r - 1) \; e^{-\frac{P_0}{Ar} t},$$

MOD. DJPS 4 (A 4) · 3000 · 2-48

and has its maximum value for $t = 0$, being

$$\left[\frac{dx}{dt}\right]_{t=0} = \frac{x_0\ P_0}{Ar}\ (r - 1).$$
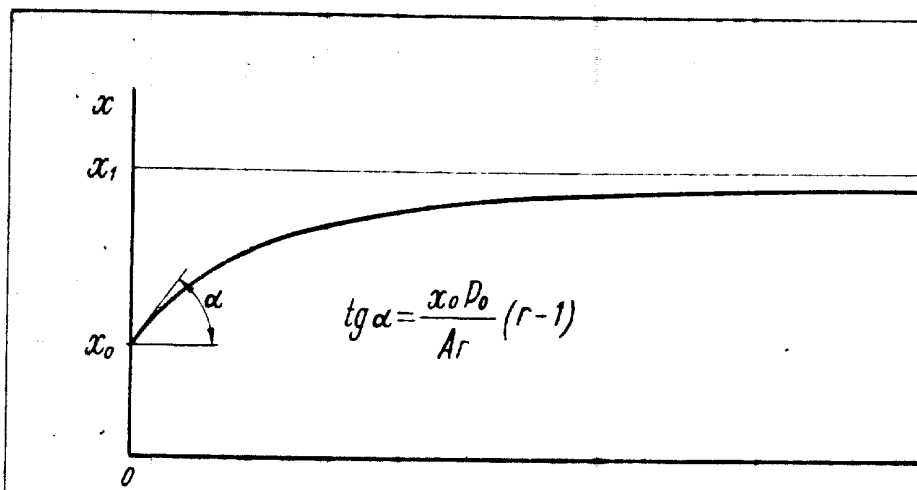

$$tg\,\alpha = \frac{x_0\,P_0}{Ar}\,(r-1)$$

Fig. 1.

Fig. 1 represents the worked out solution. After concentration has reached value x_1, we may say, from the point of view of heavy water selection, that the cell has reached its "regimen".

2. Heavy water concentration in a series of electrolitic cells.

Once the regimen has been reached, let $F_1 = p\ P_0$ be the constant fraction of flow P_0, which may be recovered from steam and from liquid water carried by the electrolysis-produced gases.

The D_2O concentration in the water-flow F_1 equals the one in water contained in the cell (1); its value is indeed $x_1 = rx_0$. If a second cell is fed with flow F_1, said cell being of the same type as the first but of an output reduced by the ratio p of the flow, the second cell, after the regimen has been reached, will on its turn yield a flow $F_2 = p\ F_1 = p^2 P_0$, in which the D_2O concentration will be $x_2 = r\ x_1 = r^2\ x_0$.

---

(1) In the range of low concentrations the influx of the fact that the vapour tension of D_2O is lower than that of H_2O need not to be taken into account.

MOD. DJPS 4 (A 4) · 3000 · 2-48

Thus proceeding, we may connect in a series n cells (1) of the same type, but of a flow decreasing by ratio p ; from the last cell the flow

$$P_n = p^n P_2$$

shall be obtained, having

$$x_n = r^n x_o$$

as a concentration, and the n cells will furnish eventually a total concentration ratio equal to r^n . (Fig.2).

Calling η the ratio between the obtained heavy water and the one fed to the system (efficiency of the system), it results:

$$\eta = \frac{p^n P_o \; r^n x_o}{P_o \; x_o} = (pr)^n.$$

As necessarily $\eta < 1$, therefore is $pr < 1$, whichever type the cells in question may be.

Finally, if W_1, is the electric power absorbed by the first cell, the total power W absorbed by the system of n cells is

$$W = W_1 (1 + p + p + \ldots + p^{n-1}).$$

The number n of necessary cells to reach a given concentration may be obtained by establishing the relative value of the total concentration ratio r^n. If we call this ratio k, it is

$$n = \frac{\log k}{\log r} ,$$

and the number nearest to the resulting value of n shall be chosen.

In Fig.2, if we take into consideration a cell having place i , coefficients q and t represent respectively : q the fraction of flow i_{i-1} which is electrolized;

---

(1) Each "cell" thus defined may in practice be constituted by a number decreasing by ratio p of similar individual cells.

t the fraction of flow P_{i-1} which is lost on account of :
1) overflow or the like, 2) evaporation in the room space,
and 3) which cannot be recovered from the steam and the
liquid water carried by the electrolysis-produced gases;
the relations

$$p + q + t = 1,$$

$$p + t = s,$$

are valid.

3. Recovery of deuterium contained in the hydrogen produced by electrolysis.

Let us imagine to burn the hydrogen produced by the
first, second, ..., n-th cell. Progressively decreasing
amounts of water will be obtained, given respectively by

$$q\,P_o, \qquad q\,P_1 = qp\,P_o, \quad \ldots\ldots\ldots, \quad q\,P_n = qp\,P_o,$$

the progressively increasing D_2O concentrations of which will
be furnished by the

$$\frac{x_1}{s} = \frac{r x_o}{s}, \quad \frac{x_2}{s} = \frac{r^2 x_o}{s}, \quad \ldots\ldots\ldots, \quad \frac{x_o}{s} = \frac{r^n x_o}{s}$$

respectively.

It is to be noticed that the concentration ratio of
said flows between one cell and the next is still r.

Having experimentally ascertained th t r s, water
obtained by burning the hydrogen coming from the first cells
would have a D_2O concentration lower than the one of natural
water, so that this synthetic water would not be fit to feed
any of the cells.

It might be advantageous, on the contrary, to burn
hydrogen produced by the last cells, for which

$$r^i \qquad s \qquad (i = n,\ n-1,\ \ldots\ldots),$$

and add the synthetic water thus obtained to the feeding of
those among the precedent cells, which are fed with water having
a D_2O concentration equal to, or not much different from r^i/s .

Fig.3 shows, as a function of the position number of
the cells, the values of the concentrations

$$x_i, \quad \frac{x_i}{s} \qquad (\ i = n,\ n - 1,\ \ldots\ldots).$$

MOD DJPS 4 (A 4) 3000 2-48

$$q p_0 \quad \nearrow \frac{x_1}{s}$$

$$q p_1 \quad \nearrow \frac{x_2}{s}$$

$$q p_{n-2} \quad \nearrow \frac{x_{n-1}}{s}$$

$$q p_{n-1} \quad \nearrow \frac{x_n}{s}$$

$$p_0 \rightarrow \boxed{x_1} \quad \frac{p_1 = p\, p_0}{x_1 = r\, x_0} \rightarrow \boxed{x_2} \quad \frac{p_2 = p^2 p_0}{x_2 = r^2 x_0} \rightarrow \quad \frac{p_{n-2} = p^{n-2} p_0}{x_{n-2} = r^{n-2} x_0} \rightarrow \boxed{x_{n-1}} \quad \frac{p_{n-1} = p^{n-1} p_0}{x_{n-1} = r^{n-1} x_0} \rightarrow \boxed{x_n} \quad \frac{p_n = p^n p_0}{x_n = r^n x_0} \rightarrow$$

$$x_1 \quad \searrow t\, p_0$$

$$x_2 \quad \searrow t\, p_1$$

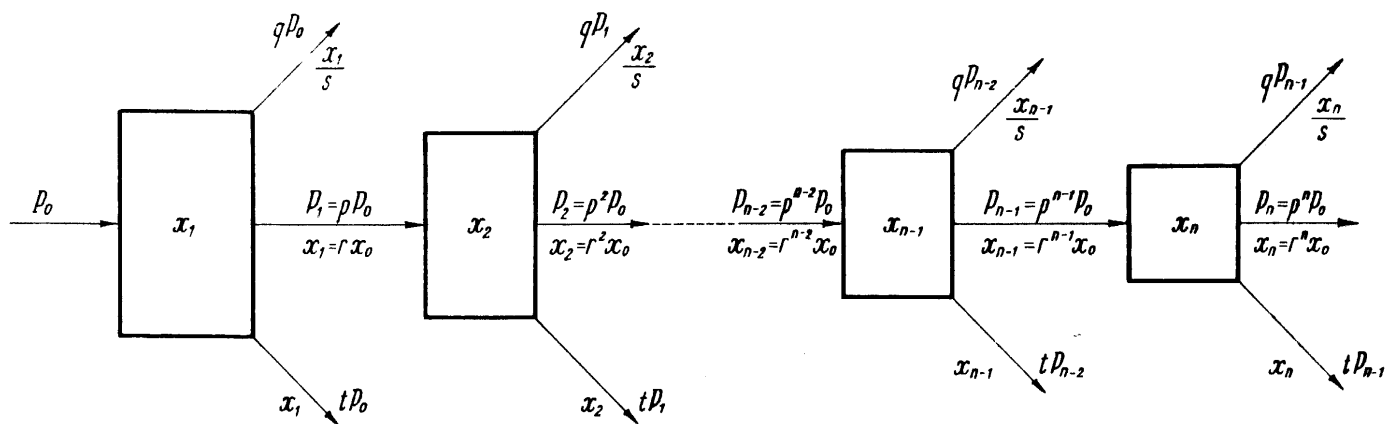$$x_{n-1} \quad \searrow t\, p_{n-2}$$
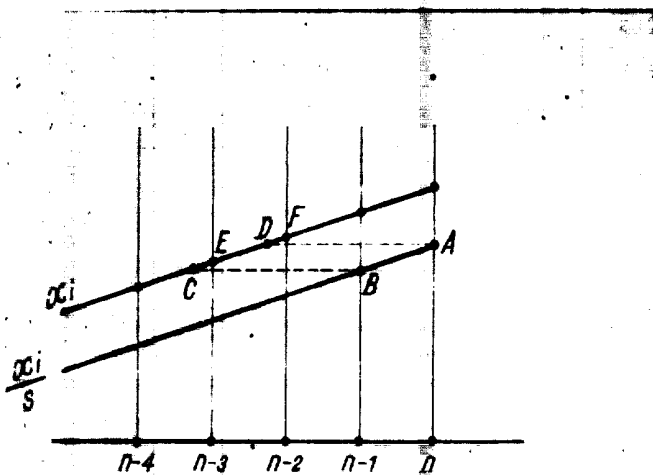
$$x_n \quad \searrow t\, p_{n-1}$$

Fig.2.

Fig.3.

Let us imagine that the burning of hydrogen coming from the last two cells n, n-1 has been decided upon. From points A and B, which give the concentrations x_n/s and x_{n-1}/s corresponding to the synthetic waters obtained from the two cells, let us draw horizontal lines AD, BC until the curve of concentrations x_i is met in D and C. As on said curve point D nears point F which represents the concentrations x_{n-2}, and point C nears point E, which represents the concentration x_{n-3}, it will be of advantage to supply the additional feeding

- to the (n-1)-th cell with water obtained from hydrogen of the n-th cell;

- to the (n-2)-th cell with water obtained from hydrogen of the (n-1)th cell,

as shown in Fig.4.

The feeding of (n-1)th and (n-2)th cells is thus increased, and by consequence the feeding of the nth cell too.

While before this added feeding to cells (n-1)th and (n-2)th the flows deriving from the combustion of hydrogen produced by cells nth and (n-1)th are respectively

$$ q_D \quad \overset{n-1}{F_e}, \qquad q_D \quad \overset{n}{F_e}, $$

after the added feeding has been provided, said flows assume values z, y which are obtained by solving the equations (Fig.4) :

MOD. DJPS 4 (A 4) - 3000 - 2-48

$$\left(\begin{array}{l} y = qp\ (p^{n-3}\ P_o + z) \\ \\ z = qp\ (p(p^{n-3}P_o + z), \end{array}\right.$$

that is to say

$$\left(\begin{array}{l} y = \dfrac{p^{n-2}\ q}{1-2\ pq}\ P_o \\ \\ z = \dfrac{p^{n-1}\ q}{1-2\ pq}\ P_o\ . \end{array}\right.$$
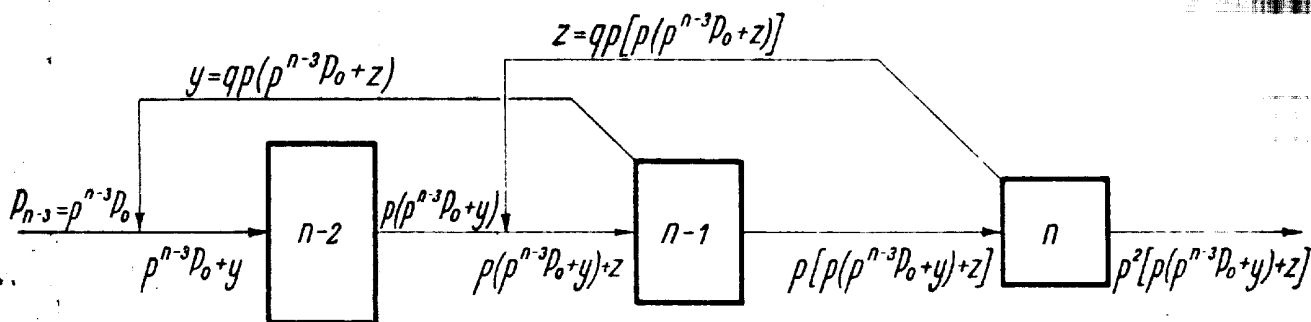

Fig.4.

The output of the last cell will be

$$P_n = p^n\ P_o\ \left(\ 1 + \dfrac{2\ pq}{1 - 2\ pq}\ \right),$$

so that the final output increase obtained by burning the hydro-gen of the last two cells is given by

$$P_n - p^n P_o\ =\ \dfrac{2p^{n+1}\ q}{1-2\ pq}\ P_o,$$

while ratio $P_n/p^n P_o$ comes from the

MOD. DJPS 4 (A 4) · 3000 · 2-48

$$\frac{\overline{P}_n}{p^n P_o} = 1 + \frac{2\ pq}{1-2\ pq}$$

By the same ratio the amount of produced D_2O will be increased, insofar as the additional feeding does not alter the concentrations in the least.

As a consequence of this feeding, the three last cells will absorb more power, according to the same ratio as the fed flows.

If we call $\overline{W}_{n-2}$, $\overline{W}_{n-1}$, $\overline{W}_n$ the new absorbed power, it will be:

$$\overline{W}_{n-2} = \frac{p^{n-3}P^o+y}{p^{n-3}P_o}\ W_{n-2} = (1+\frac{pq}{1-2\ pq})\ W_{n-2},$$

$$\overline{W}_{n-1} = (1+\frac{2\ pq}{1-2\ pq})\ W_{n-1}$$

$$\overline{W}_n = (1+\frac{2\ pq}{1-2\ pq})\ W_n$$

The system of n cells will absorb, as a consequence of the additional feeding, more power, and precisely

$$(\overline{W}_{n-2}- W_{n-2}) + (\overline{W}_{n-1} - W_{n-1}) + (\overline{W}_n - W_n) =$$

$$= (p^{n-2} + 2\ p^{n-1} + 2\ p^n)\ \frac{q}{1-2\ pq}\ W_1 .$$

As an effect of additional feeding the D_2O efficiency of the system takes the value

$$\eta = \frac{p^2\left(p(p^{n-3}P_o+y) + z\right) r^n x_o}{P_o\ x_o}$$

$$= (pr)^n + \frac{2\ p^{n+1}qr^n}{1-2\ pq}$$

$$= \eta\ (1+\frac{2\ pq}{1-2\ pq}),$$

MOD. DJPS 4 (A 4) · 3000 · 2·48

and the efficiency increase is

$$\bar{\eta} - \eta \quad = \quad \frac{2p^{n+1} qr^n}{1-2 \ pq} \quad .$$

4. Conclusion.

Numerous measurements taken over a number of years in water electrolysis plants have fully confirmed the above considerations. Said measurements have also permitted to establish the numeric values of the constants met with in this paper.

S U M M A R Y.

In an electric cell a selection between H_2O and D_2O takes place. The behaviour of a single cell and the behaviour of a series of cells are successively examined. The recovery of deuterium contained in the hydrogen produced by the last cells of the series is considered too.

Numerous measurements have confirmed the above descripted considerations.